meta-Cycloparaphenylenes (*m*CPPs) with pendant carborane

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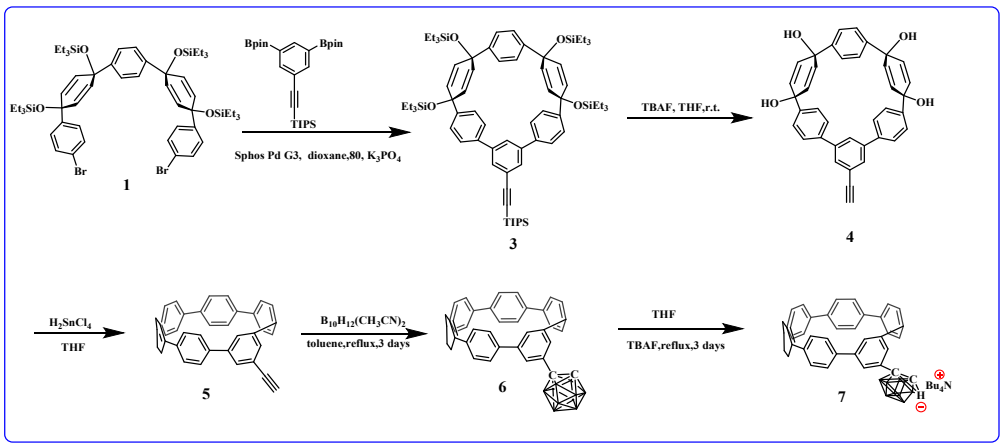
CONTENTS

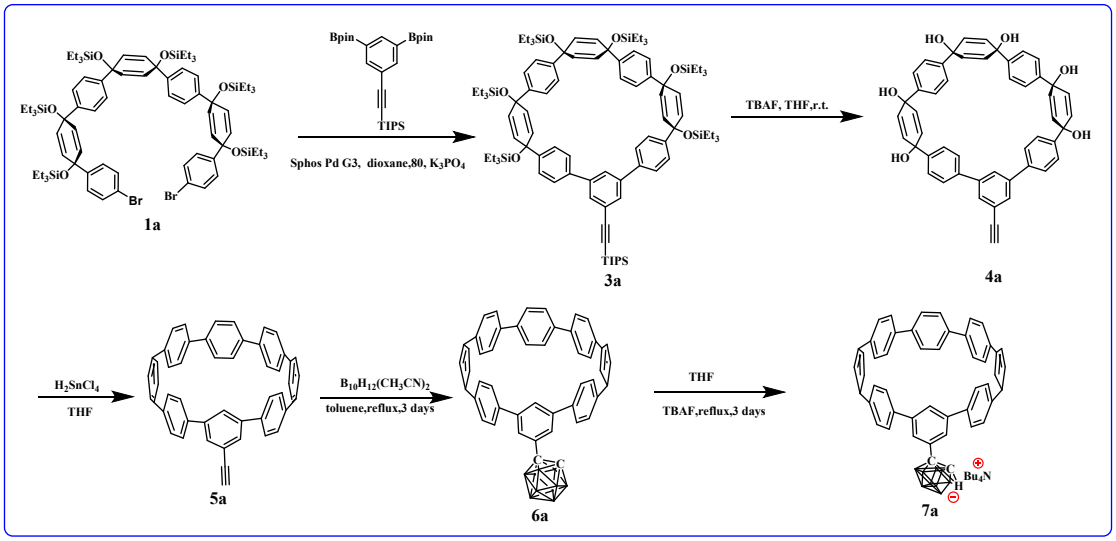
I. General method

In this work, all the synthetic steps were carried out under an inert argon atmosphere using standard Schlenk and glovebox techniques. Commercial reagents were used without any further purification after purchasing. THF and toluene were distilled on sodium / benzophenone. (1), (3), (4), (5), (1a) were synthesized according to literature procedures. [S1] $B_{10}H_{12}(CH_3CN)_2$ was synthesized by a modified method according to literature reports.[S2] NMR spectra (^1H−, ^{13}C−, and ^{11}B−) were recorded on DRX−400 and DRX−500 at ambient temperature. $CDCl_3$ was used as deuterated reagent unless specified. Mass spectra were measured with ESI−MS and APCI-HRMS (LCQ Fleet, Thermo Fisher Scientific). The UV-vis absorption spectra were obtained by SHIMADZU UV-2600. Photoluminescence spectra and decay curves were obtained by using Edinburgh FLS980 fluorescence spectrophotometer equipped with a 450 W xenon arc lamp, a picosecond pulsed LED (EPLED-380) and a microsecond flash-lamp (μF900). The decay curves were fitted by F980 software determined from a multi-exponential function: $R(t) = \sum B_i exp(-t/\tau_i)$. The absolute photoluminescence quantum yields of compounds were collected on FLS980 with integrating sphere and a supplied reference plug was used as a reference sample. Photoluminescence spectra and excitation-emission maps were measured on the HITACHI fluorescence spectrophotometer F-4700.

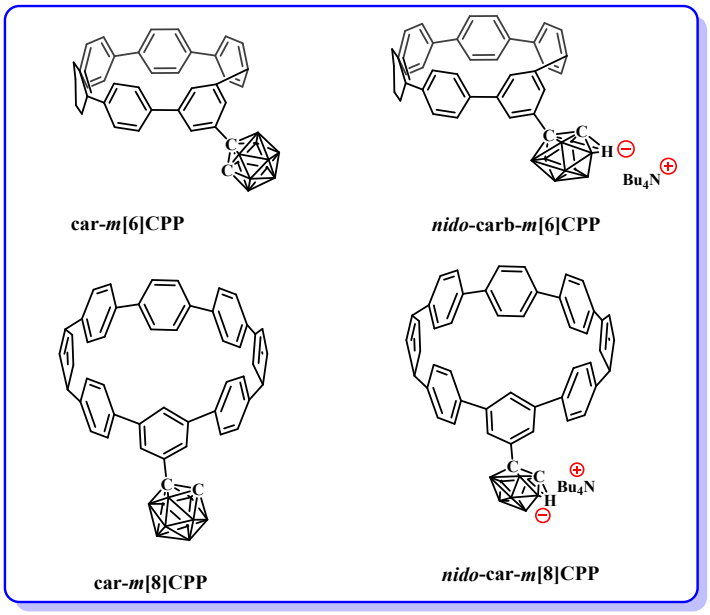
II. Synthesis



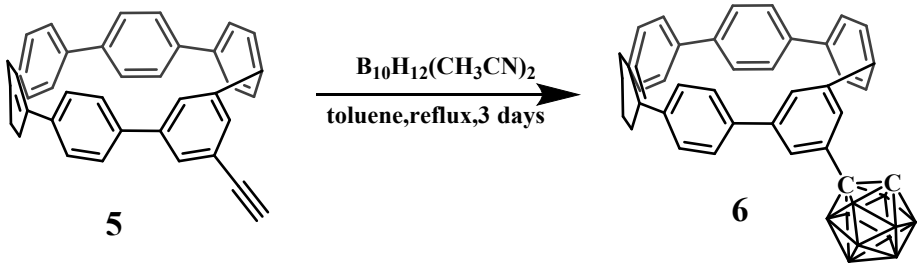
Scheme S1. The synthetic routes towards **car-*m*[6]CPP** and ***nido*-car-*m*[6]CPP**.



Scheme S2. The synthetic routes towards **car-*m*[8]CPP and *nido*-car-*m*[8]CPP**.

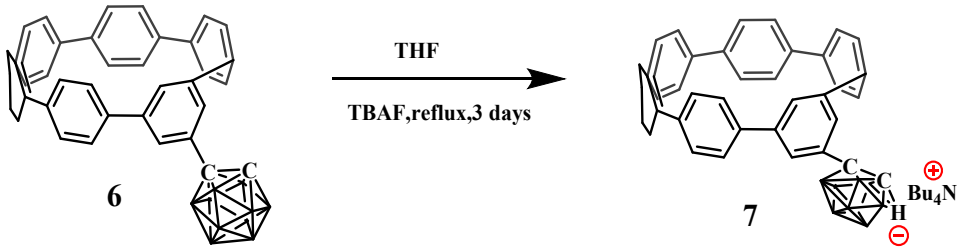


Scheme S3. The structure and identification of the compounds involved in this paper.

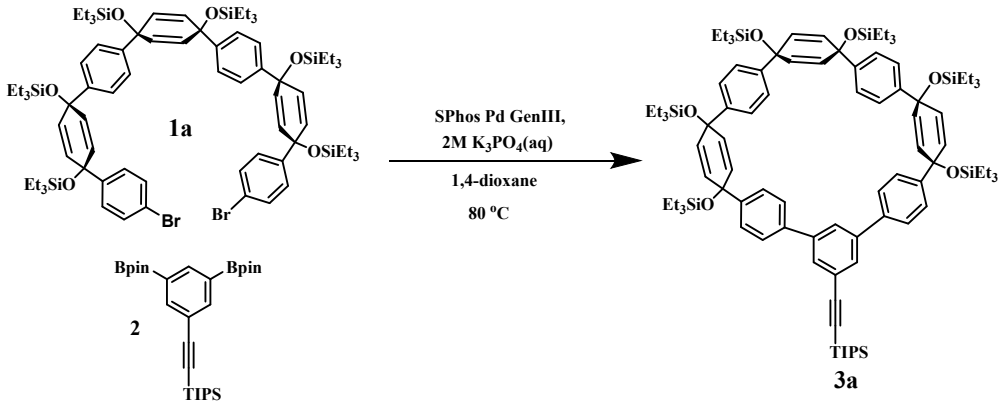


6：To a toluene solution (60 mL) of 5 (100 mg, 0.2 mmol, 1 equiv), $B_{10}H_{12}(CH_3CN)_2$ (0.21 g, 1.0 mmol, 5 equiv) was added at room temperature. The resulting reaction mixture was refluxed for

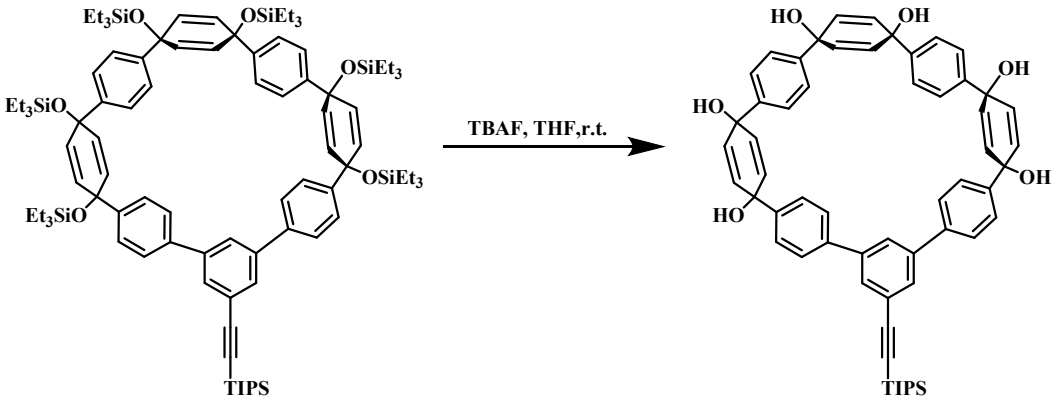
three days. MeOH (20 mL) was then added to quench the reaction. Excessive solvent was removed under vacuum, and the resulting solid was filtered and dissolved in CH_2Cl_2. After removal of solvent, an orange red solid was afforded. The product was purified by automated flash alumina gel chromatography (30% to 60% dichloromethane in petroleum ether) to give **6** as a yellow solid (74 mg, 60%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 1.5 Hz, 2H), 7.46 – 7.37 (m, 16H), 7.10 (d, *J* = 8.6 Hz, 4H), 5.61 (s, 1H), 4.08 (s, 1H). ^{13}C NMR (126 MHz, Methylene Chloride-d^2) δ 143.57, 141.69, 141.28, 139.84, 138.07, 137.10, 136.68, 134.92, 129.94, 128.61, 128.43, 128.31, 128.01, 122.02, 77.48, 61.09, 1.32. ^{11}B NMR (160 MHz, Methylene Chloride-d^2) δ -3.23(2B), -5.49(2B), -9.97(2B), -12.68(2B) (d, *J* = 329.0 Hz). APCI−MS (m/z): Calcd for $C_{38}H_{34}B_{10}$ 598.3664, found 598.3617.



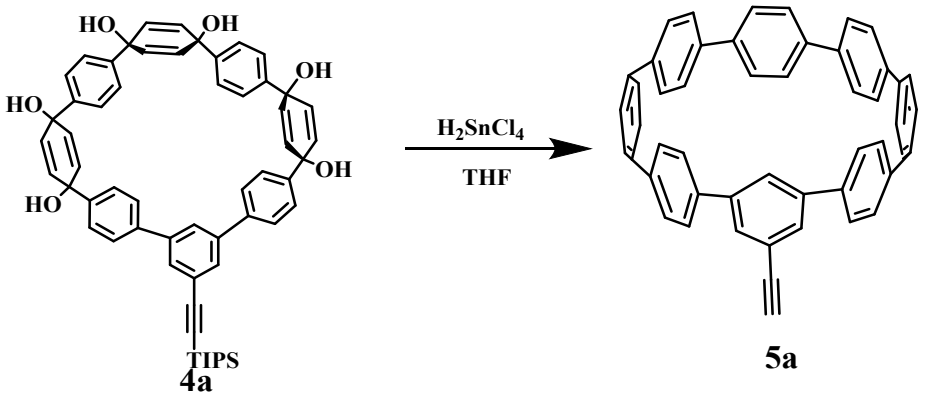
7. Tetrahydrofuran (40 mL) was added to the 100 mL scintillation vial containing 6 (50 mg, 0.0834 mmol, 1 equiv) and the vial was equipped with a stir bar and septa. Tetra-n-butylammonium fluoride (0.42 mL, 0.42 mmol, 5 equiv, 1 M in tetrahydrofuran) was added to the reaction flask and the resulting reaction mixture was refluxed for three days. The reaction mixture was allowed to cool to room temperature. Excessive solvent was removed under vacuum, and the resulting solid was filtered and dissolved in CH_2Cl_2. After removal of solvent, a yellow solid was afforded. The product was purified by automated flash alumina gel chromatography (30% to 60% dichloromethane in petroleum ether) to give **7** as a yellow solid.^{1}H NMR (500 MHz, Acetone-d_6) δ 7.54 (s, 4H), 7.49 (d, *J* = 9.1 Hz, 4H), 7.45 – 7.39 (m, 8H), 7.36 (d, *J* = 1.7 Hz, 2H), 7.15 (dq, *J* = 7.6, 2.2 Hz, 4H), 5.38 (t, *J* = 1.7 Hz, 1H), 3.45 – 3.35 (m, 8H), 2.34 (s, 1H), 1.84 – 1.75 (m, 8H), 1.46 – 1.33 (m, 8H), 0.95 (t, *J* = 7.4 Hz, 12H), -2.34 (s, 1H). ^{13}C NMR (126 MHz, Acetone-d^6) δ 149.10, 144.06, 142.56, 139.47, 138.27, 137.38, 137.06, 135.91, 130.10, 129.02, 128.79, 128.40, 128.06, 121.31, 68.03, 59.38, 26.13, 24.37, 20.35, 13.85. ^{11}B NMR (160 MHz, Acetone-d^6) δ -9.31(1B), -11.05(1B), -14.53(1B) (d, *J* = 36.9 Hz), -17.47(1B), -18.65(1B), -20.41(1B), -23.68(1B), -33.45(1B), -36.50(1B). ESI−MS (m/z): Calcd for $C_{38}H_{33}B_9$ 587.3456, found 587.3606.



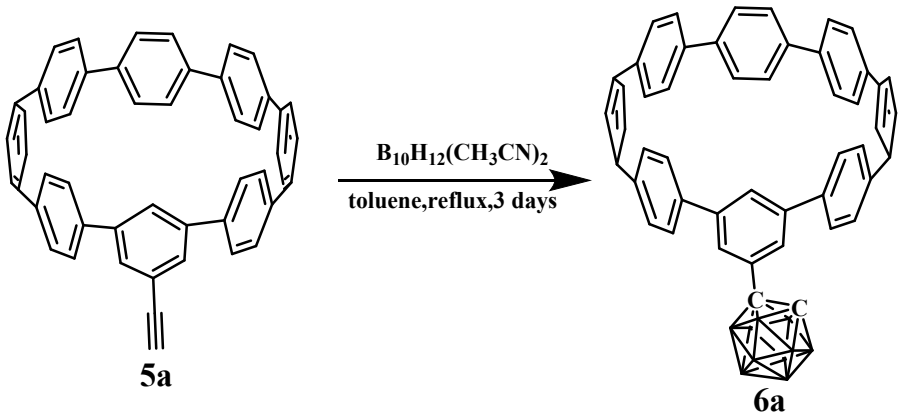
3a. 1a (2.5 g, 1.69 mmol, 1 equiv), 2 (1.03 g, 2.0 mmol, 1.2 equiv) and Sphos Pd Gen III (132 mg, 0.169 mmol, 0.1 equiv) were added to a 500 mL round bottom flask equipped with a stir bar. The flask was evacuated (5 minutes) and purged with nitrogen 5 times. 1,4-dioxane and K_3PO_4 were sparged for at least 1 hour prior to use. The round bottom flask was equipped with a septum and 1,4-dioxane (280 mL) was added to the round bottom flask and the solution was sparged for 30 minutes. The round bottom flask was placed in a preheated oil bath (80 °C) for 10 minutes then K_3PO_4 (40 mL, 2 M in deionized water) was added. The reaction was allowed to stir at 80 °C overnight. The reaction mixture was allowed to cool to room temperature. It was then filtered through a fritted suction funnel of Celite. The round bottom flask was rinsed with dichloromethane and filtered through the Celite plug. The filtrate was added to a separatory funnel along with deionized water (20 mL) and the product was extracted (3 x 100 mL) with ethyl acetate. The organic layers were dried over sodium sulfate and concentrated to yield the crude product as a brown solid. The product was purified by automated flash silica gel chromatography (0% to 40% ethyl acetate in petroleum ether) to give the product as a white solid (2.0 g, 75%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 1.6 Hz, 2H), 7.64 (s, 1H), 7.53 (d, *J* = 8.4 Hz, 4H), 7.43 (q, *J* = 8.2 Hz, 11H), 6.17 (s, 4H), 6.05 (d, *J* = 10.1 Hz, 4H), 5.93 (d, *J* = 10.1 Hz, 4H), 3.71 (s, 1H), 1.16 (s,21H), 1.03 – 0.86 (m, 54H), 0.69 (q, *J* = 7.9 Hz, 12H), 0.59 – 0.47 (m, 24H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 146.26, 145.90, 145.74, 141.20, 138.73, 133.03, 131.99, 131.12, 128.58, 127.30, 126.85, 126.14 (d, *J* = 7.1 Hz), 125.93, 124.50, 107.27, 90.74, 71.64, 70.98, 69.69, 67.24, 27.06, 18.86, 11.49, 7.50 – 6.96 (m), 6.84 – 6.33 (m).



4a. Tetrahydrofuran (40 mL) was added to the 100 mL scintillation vial containing 3a (2.0 g, 1.26 mmol, 1 equiv) and the vial was equipped with a stir bar and septa. Tetra-n-butylammonium fluoride (12.6 mL, 12.6 mmol, 10 equiv, 1 M in tetrahydrofuran) was added to the reaction flask and this was allowed to stir for 2 hours at room temperature. Deionized water (20 mL) was added and the organic solvent was removed via rotavapor. The solid was collected by suction filtration and rinsed with dichloromethane to yield the product as a white solid. The crude product was used as is for the following reaction.

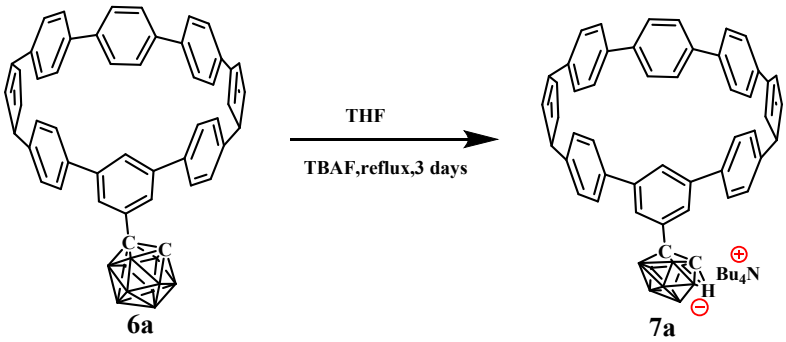


5a. $SnCl_2$•H_2O (181 mg, 0.80 mmol) was added to a 100 mL round bottom flask equipped with a stir bar and septum. Tetrahydrofuran (20 mL) was added followed by hydrochloric acid (0.13 mL, 1.6 mmol, 12 M). This was allowed to stir at room temperature for 30 minutes. H_2SnCl_4 solution (15 mL, 0.58 mmol, 2.2 equiv, 0.04 M) was added to the scintillation vial containing 4a (231.7 mg, 0.26 mmol, 1 equiv) and the reaction was allowed to stir for 1 hour at room temperature. The reaction was quenched with saturated sodium bicarbonate (20 mL) and the product was extracted with dichloromethane (3 x 20 mL). The organic layers were washed with brine (1 x 50 mL), dried over sodium sulfate and concentrated to give the crude product as a white solid. The product was purified by automated flash alumina gel chromatography (0% to 50% dichloromethane in petroleum ether) to give **5a** as a yellow solid (82 mg, 50% two steps). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 1.7 Hz, 2H), 7.53 – 7.46 (m, 16H), 7.43 – 7.37 (m, 8H), 7.32 (d, *J* = 8.4 Hz, 4H), 6.35 (t, *J* = 1.7 Hz, 1H), 3.18 (s, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 142.85, 140.41, 140.15, 138.64, 138.44, 138.19, 137.90, 137.53, 136.77, 128.82, 127.87, 127.67, 127.51, 127.31, 123.02, 83.88, 77.52. APCI−MS (m/z): Calcd for $C_{50}H_{32}$ 632.2504, found 632.2493.



6a：To a toluene solution (60 mL) of 5a (136 mg, 0.21 mmol,1 equiv), $B_{10}H_{12}(CH_3CN)_2$ (0.22 g, 1.07 mmol,5 equiv) was added at room temperature. The resulting reaction mixture was refluxed for three days. MeOH (20 mL) was then added to quench the reaction. Excessive solvent was removed under vacuum, and the resulting solid was filtered and dissolved in CH_2Cl_2. After removal of solvent, an orange red solid was afforded. The product was purified by automated flash alumina gel chromatography (0% to 30% dichloromethane in hexanes) to give **6a** as a yellow solid (110 mg, 68%). The solubility of the product was poor and its nuclear magnetism was not characterized. ^{11}B NMR (160 MHz, Chloroform-*d*) δ -5.80. APCI−MS (m/z): Calcd for $C_{50}H_{42}B_{10}$

750.4290, found 750.4319.



7a. Tetrahydrofuran (40 mL) was added to the 100 mL scintillation vial containing 6a (100 mg, 0.133 mmol, 1 equiv) and the vial was equipped with a stir bar and septa. Tetra-n-butylammonium fluoride (0.67 mL, 0.67 mmol, 5 equiv, 1 M in tetrahydrofuran) was added to the reaction flask and the resulting reaction mixture was refluxed for three days. The reaction mixture was allowed to cool to room temperature. Excessive solvent was removed under vacuum, and the resulting solid was filtered and dissolved in CH_2Cl_2. After removal of solvent, a yellow solid was afforded. The product was purified by automated flash alumina gel chromatography (30% to 60% dichloromethane in petroleum ether) to give 7a as a yellow solid.^{1}H NMR (500 MHz, Acetone-d_6) δ 7.75 – 7.61 (m, 13H), 7.55 (d, J = 9.4 Hz, 12H), 7.38 (d, J = 7.6 Hz, 5H), 6.11 (s, 1H), 3.53 – 3.41 (m, 8H), 2.47 (s, 1H), 1.86 (p, J = 7.7 Hz, 8H), 1.55 – 1.40 (m, 8H), 1.02 (t, J = 7.0 Hz, 12H), -2.26 (s, 1H).^{13}C NMR (126 MHz, Acetone-d^6) δ 148.89, 142.73, 142.27, 139.92, 139.41, 138.70, 138.44, 138.10, 132.87, 129.48, 128.43 (d, J = 7.9 Hz), 128.16, 122.68, 59.38, 27.33, 24.38, 20.36, 13.86. ^{11}B NMR (160 MHz, Acetone-d^6) δ -9.27(1B), -10.90(1B), -14.10(1B), -17.19(1B), -18.57(1B), -20.35(1B), -23.51(1B), -33.41(1B), -36.51(1B). ESI−MS (m/z): Calcd for $C_{50}H_{42}B_9$ 739.4082, found 739.4233.

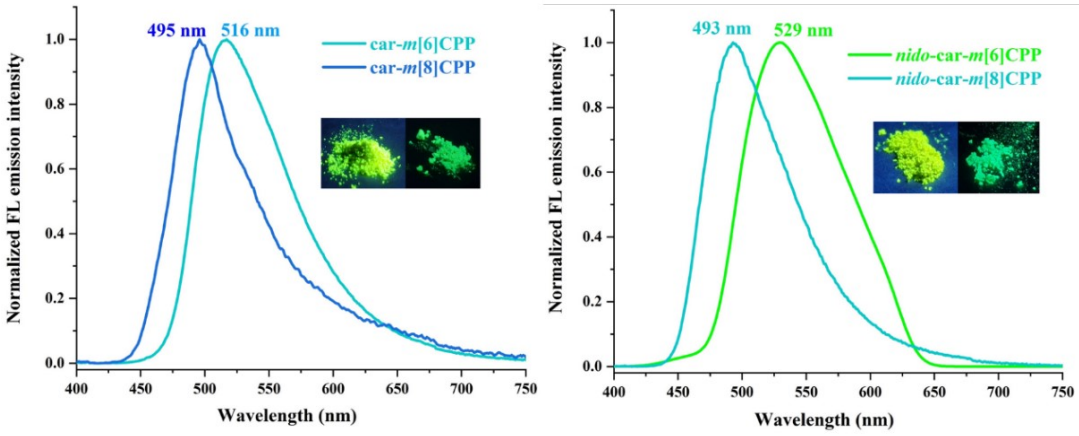


Figure S1. The FL spectra of **car-*m*[6]CPP**, **car-*m*[8]CPP**, ***nido*-car-*m*[6]CPP** and ***nido*-car-*m*[8]CPP** in solid state at room temperature.

Table S1. Photophysical properties of the carborane-substituted meta-nanohoops (*m*[n]CPPs)(In solid state).

Compound	Fluorescence		
	λ_{em}[a]/nm	Φ_{PL}[b]	τ/ns
car-*m*[6]CPP	516	11.41%	1.70
car-*m*[8]CPP	495	14.74%	1.46
***nido*-car-*m*[6]CPP**	529	15.92%	1.69
***nido*-car-*m*[8]CPP**	493	18.52%	2.10

[a] In solid state at room temperature (λ_{ex}=365 nm). [b]Absolute values.

III. Quantum yields determination: Absolute quantum yields of all compounds in THF/water or in solid state were measured by employing an integrating sphere.

The Principle of Absolute Quantum Yield Measurements

The absolute fluorescence quantum yield, η, is, by definition, the ratio of the number of photons emitted to the number of photons absorbed:

$$\eta = \frac{N^{em}}{N^{abs}} \quad (1)$$

There are two different methods for the measurement of the absolute fluorescence quantum yield: "Direct Excitation" measurements and "Direct & Indirect Excitation" measurements.

With "Direct Excitation" measurements one records the scatter and the emission of the sample being directly exited by the radiation from the excitation monochromator only, whereas with "Direct and Indirect Excitation" one also records the emission of the sample while it is in a position where it is only indirectly excited by excitation radiation bouncing within the sphere.

"Direct Excitation" Method

This method only requires two experimental setups, see figure 1.

Note that with the "Direct Excitation" method the emission measurement actually contains the information of both direct and indirect excitation, as photons that pass the sample in the direct excitation beam may still be absorbed after scattering in the sphere.

Figure 1. Two different measurement configurations required for Direct Excitation measurements:

(A) reference sample (solvent only) in sample position (1); (B) test sample in position 1 (position 2 remains empty for both measurements.)

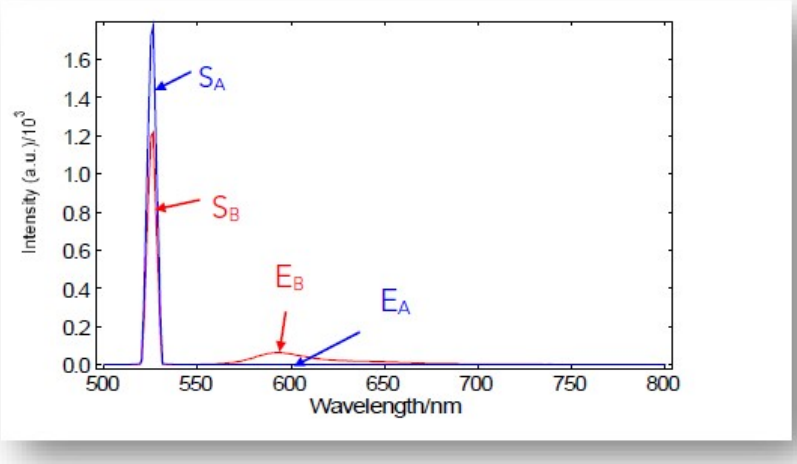


Figure 2. Spectral scans of the excitation scatter region or S-region (peaks on the left) and the emission region (E-region) of the sample and the solvent. The indices "A" and "B" refer to the experimental setup illustrated in Figure 1. Note that the quantities S_A, S_B, E_A, and E_B refer to the integral of the scans.

The absolute fluorescence quantum yield, calculated with the "Direct Excitation" method is calculated as follows:

$$\eta_{DExc} = \frac{E_B - E_A}{S_A - S_B} \qquad (2)$$

$E_A(\lambda)$ and $S_A(\lambda)$, as well as $E_B(\lambda)$ and $S_B(\lambda)$ may be measured in four individual scans. However, it is often convenient to measure these spectra in two scans only. For the calculation of the integrals, the selection of the integral regions, and the final calculation of η_{DExc} use the quantum yield wizard that is supplied with the F980 software.

If the sphere background, $E_A(\lambda)$, is sufficiently low the measurement of this region may be omitted to save measurement time. In this case the equation degrades to:

$$\eta_{DExc} = \frac{E_B}{S_A - S_B} \qquad (3)$$

IV. PL Spectra data: UV−vis absorption spectra were recorded with Shimadzu UV−3600 spectrophotometers. FL and PL spectra were recorded on a Hitachi F−7000 fluorescence spectrophotometer.

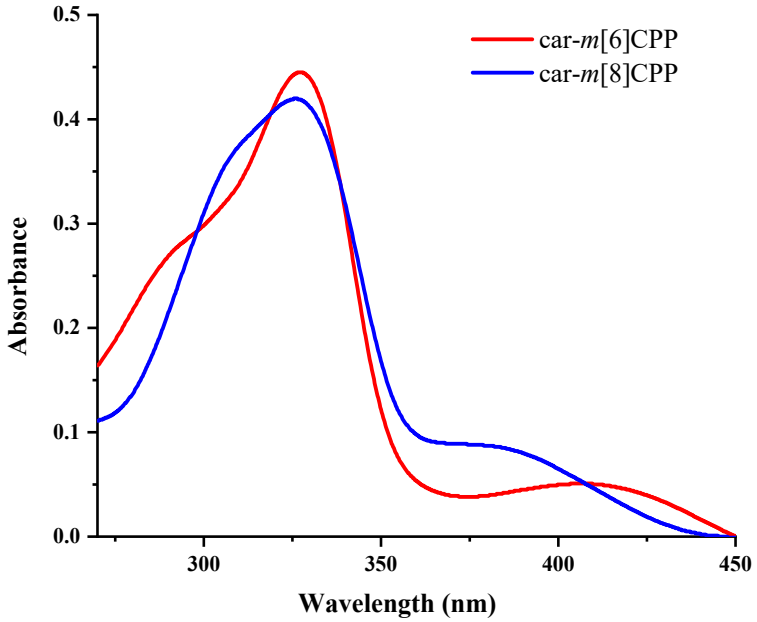


Figure S2. The absorption spectra of **car-*m*[6]CPP** and **car-*m*[8]CPP** in DCM (1.0×10^{-5} M) at room temperature.

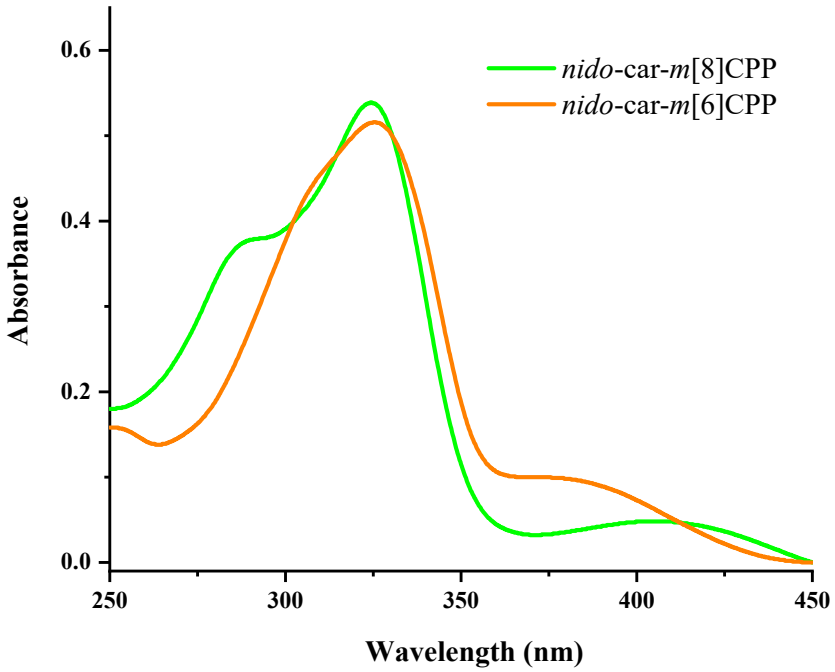


Figure S3. The absorption spectra of ***nido*-car-*m*[6]CPP** and ***nido*-car-*m*[8]CPP** in THF (1.0×10^{-5} M) at room temperature.

V. Quantum chemical calculations: Geometries of all complexes were optimized using density functional theory (DFT) method. The electronic transition energies including electron

correlation effects were computed by TD−DFT method using B3LYP functional (TD−B3LYP). The 6−31G(d, p) basis set was used to treat all atoms. All calculations described here were performed by using Gaussian 16 program.[S3]

VI. Cyclic voltammetry (CV): Electrochemical determination: Cyclic Volta metric experiments were carried out with an IM6ex (Zahner) using three electrode cell assemblies. All measurements were carried out in a one-compartment cell under Argon, equipped with a glassy-carbon working electrode, a platinum wire counter electrode, and a Ag / Ag^+ reference electrode under a scan rate of 100 mV s^{-1}. The supporting electrolyte was a 0.10 mol L^{-1} acetonitrile solution of tetrabutyl-ammonium hexafluorophosphate (Bu_4NPF_6). Each oxidation potential was calibrated with ferrocene as a reference.

Table S2. The electrochemical properties data sheet of carborane modified *m*CPPs.

Compound	E_{onset}^{ox}	HOMO (eV)	$\lambda_{cross\text{-}point}$ (nm)	LUMO（eV）	E_g（eV）
car-*m*[6]CPP	0.77	-5.57	400	-2.47	3.10
car-*m*[8]CPP	0.71	-5.51	387	-2.31	3.20
nido-car- *m*[6]CPP	0.62	-5.42	410	-2.40	3.02
nido-car- *m*[8]CPP	0.71	-5.51	395	-2.37	3.14

[a] Data in degassed CH_2Cl_2 at 298 K. [b] HOMO (eV) = −e (E_{onset}^{ox} + 4.8), E_g = 1240 / λ, LUMO (eV) = E_g + HOMO.

VII. References

[S1]: Terri C. Lovell, Curtis E. Colwell, Lev N. Zakharovb and Ramesh Jasti. *Chem. Sci.,* 2019*,* 10*,* 3786–3790.

[S2]: a) M. D. Marshall, R. M. Hunt, G. T. Hefferan, R. M. Adams and J. M. Makhlouf, J. Am. Chem. Soc. 1967, 89, 3361−3362. b) J. M. Makhlouf, W. V. Hough and G. T. Hefferan, Inorg. Chem. 1967, 6, 1196−1198. c) I. B. Sivaev, A. V. Prikaznov and D. Naoufal, Collection. of Czechoslovak. Chem. Commun. 2010, 75, 1149−1199. c) R. N. Grimes, Carboranes; 2nd ed., Vol. 9, Academic Press: New York, 2011, pp. 301–540. d) D. Power and T. R. Spalding, Polyhedron 1985, 4, 1329−1331. e) A. Toppino, A. R. Genady, M. E. El−Zaria, J. Reeve, F. Mostofian, J. Kent

and J. F. Valliant, Inorg. Chem. 2013, 52, 8743−8749. f) L. A. Galliamova, M. V. Varaksin, O. N. Chupakhin, P. A. Slepukhin and V. N. Charushin, Organometallics 2015, 34, 5285−5290.

[S3]: M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V.Bakken, C. Adamo, J. Jaram illo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision B.01, Gaussian, Inc., Wallingford CT, 2010.

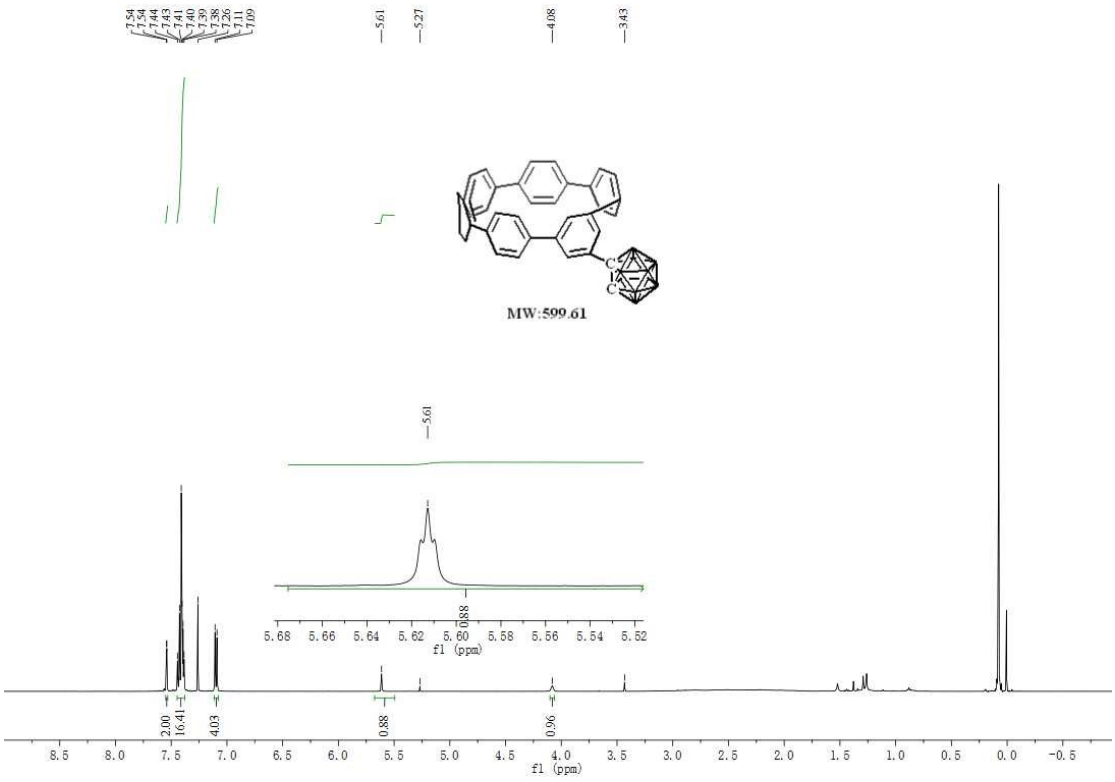


Figure S4. The ^{1}H-NMR (500 MHz, Chloroform-*d*) spectrum of compound 6.

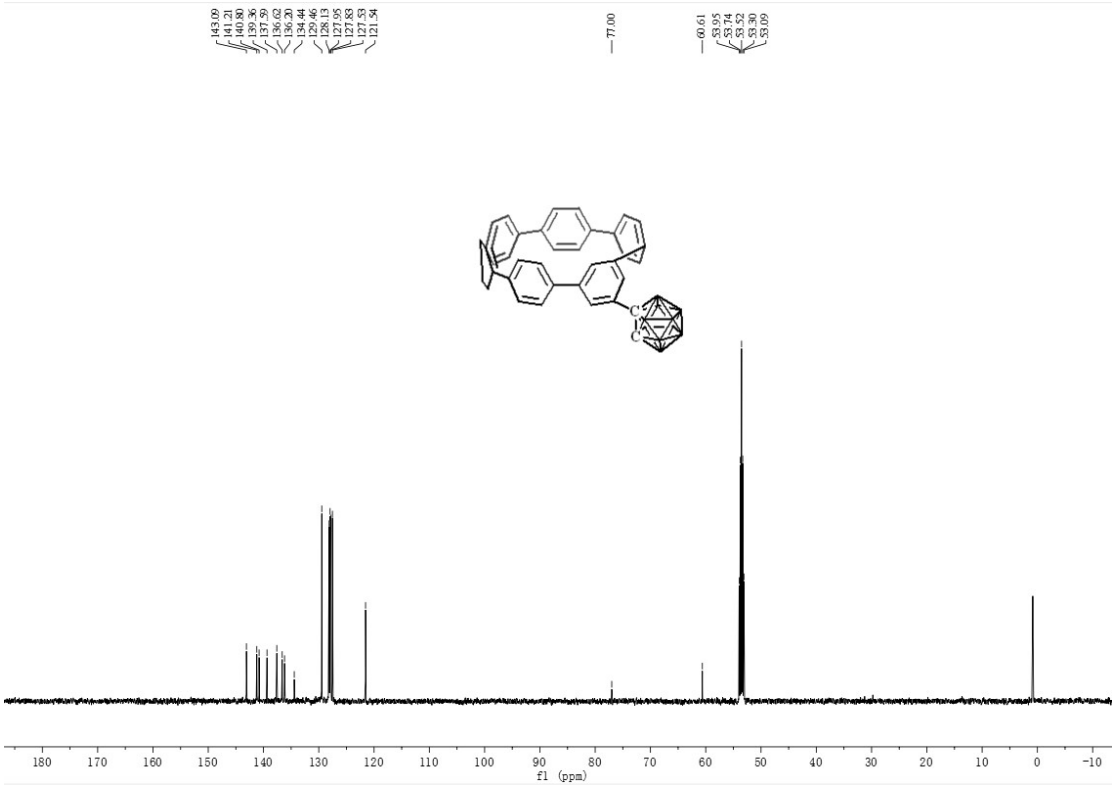


Figure S5. The ^{13}C-NMR (126 MHz, Methylene Chloride-d^2) spectrum of compound 6.

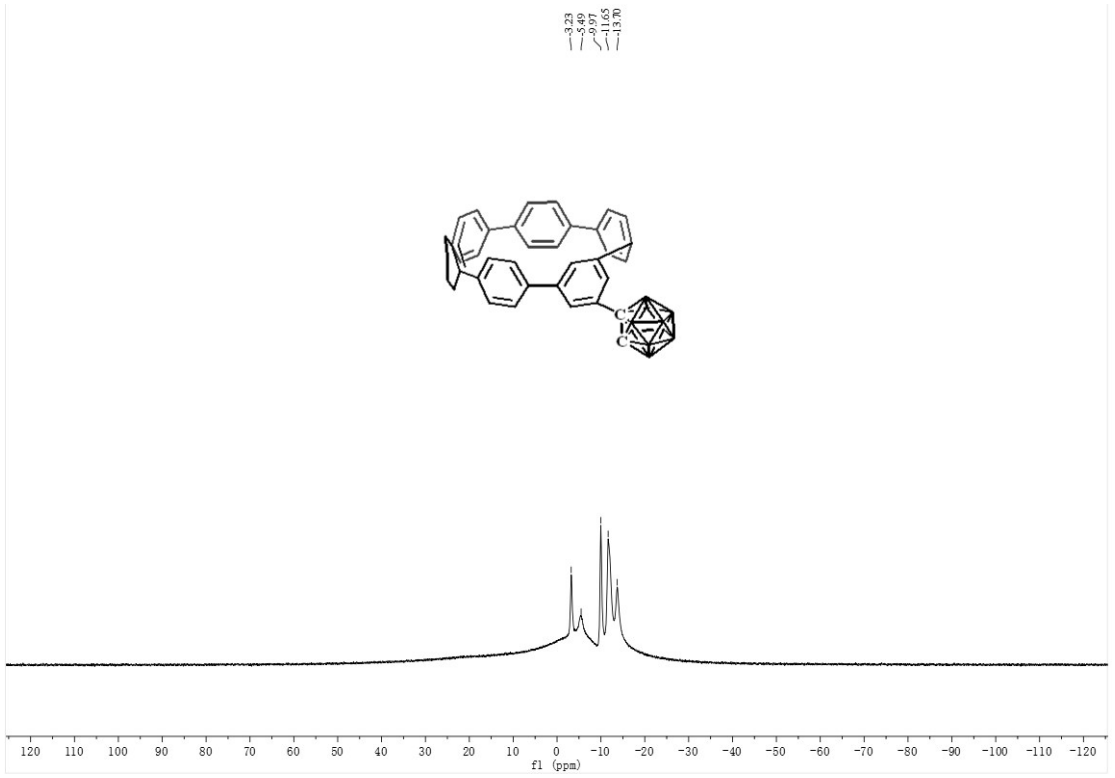


Figure S6. The ^{11}B-NMR (160 MHz, Methylene Chloride-d^2) spectrum of compound 6.

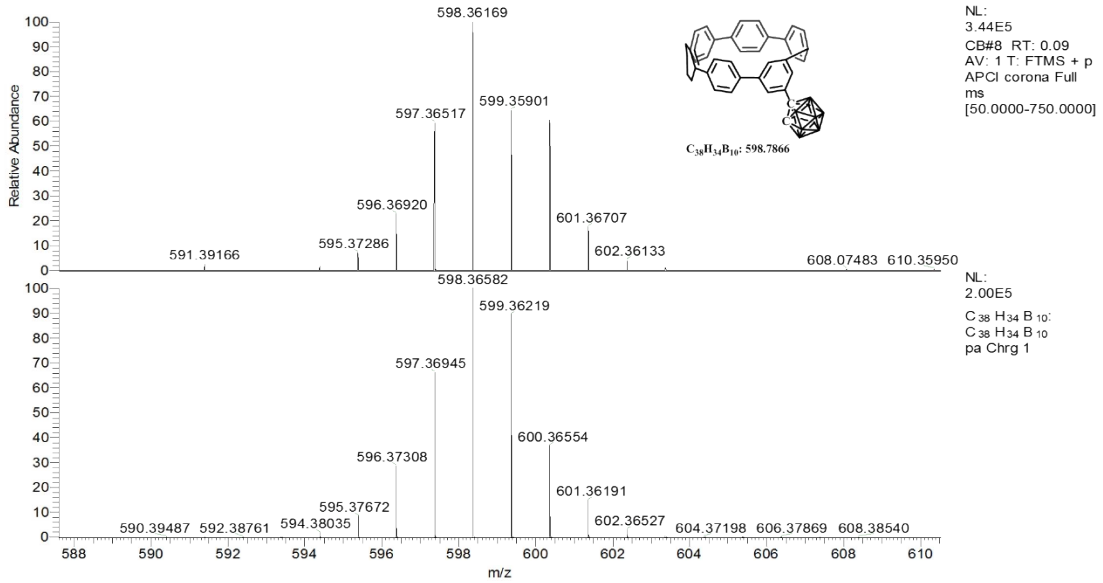


Figure.S7. The HRMS spectrum of compound 6.

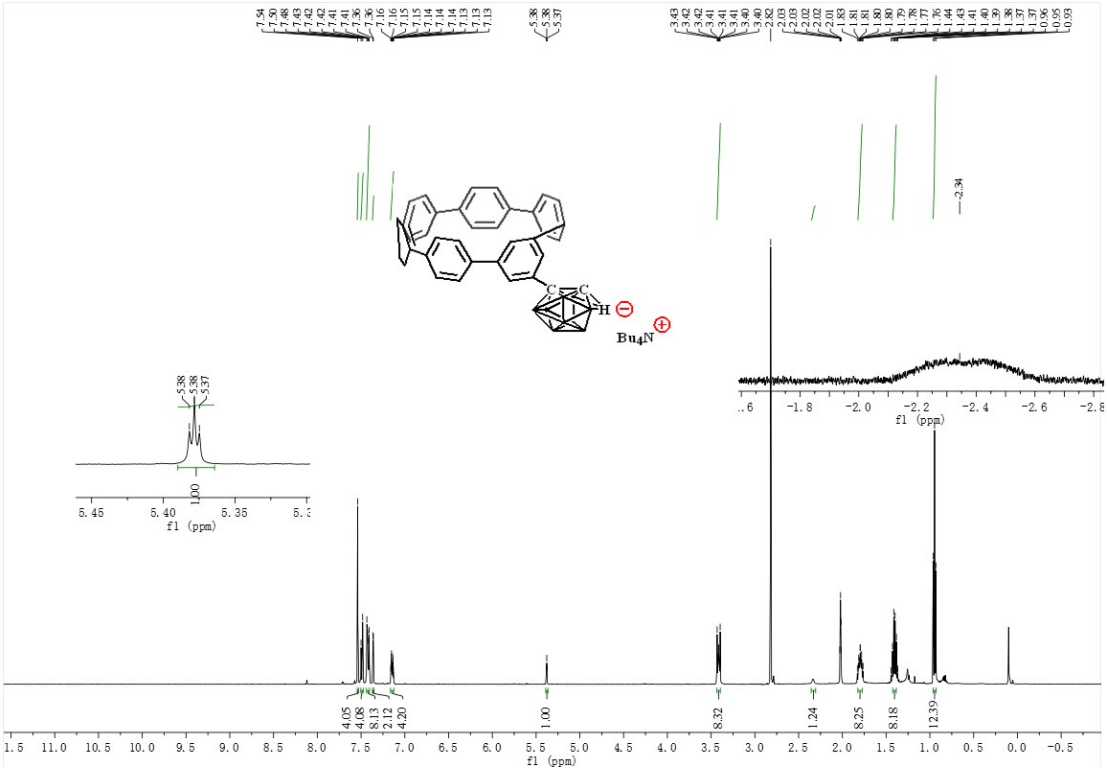


Figure S8. The ^{1}H-NMR (500 MHz, Acetone-d^{6}) spectrum of compound 7.

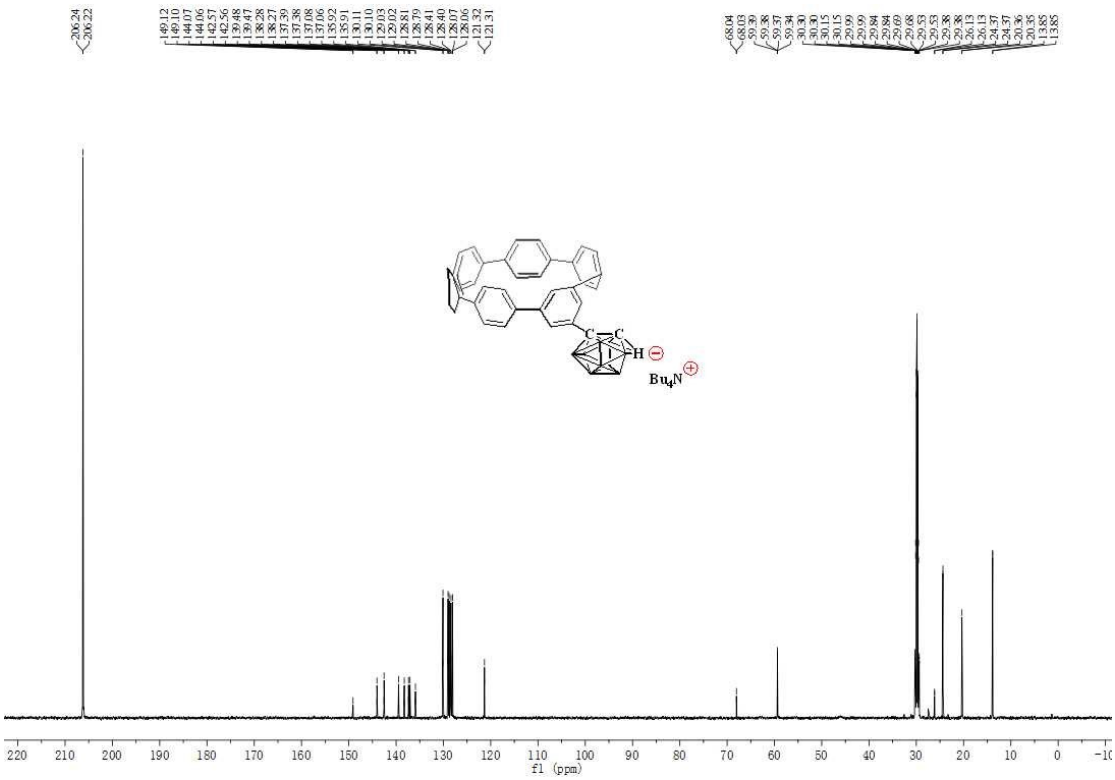


Figure S9. The ^{13}C-NMR (126 MHz, Acetone-d^6) spectrum of compound 7

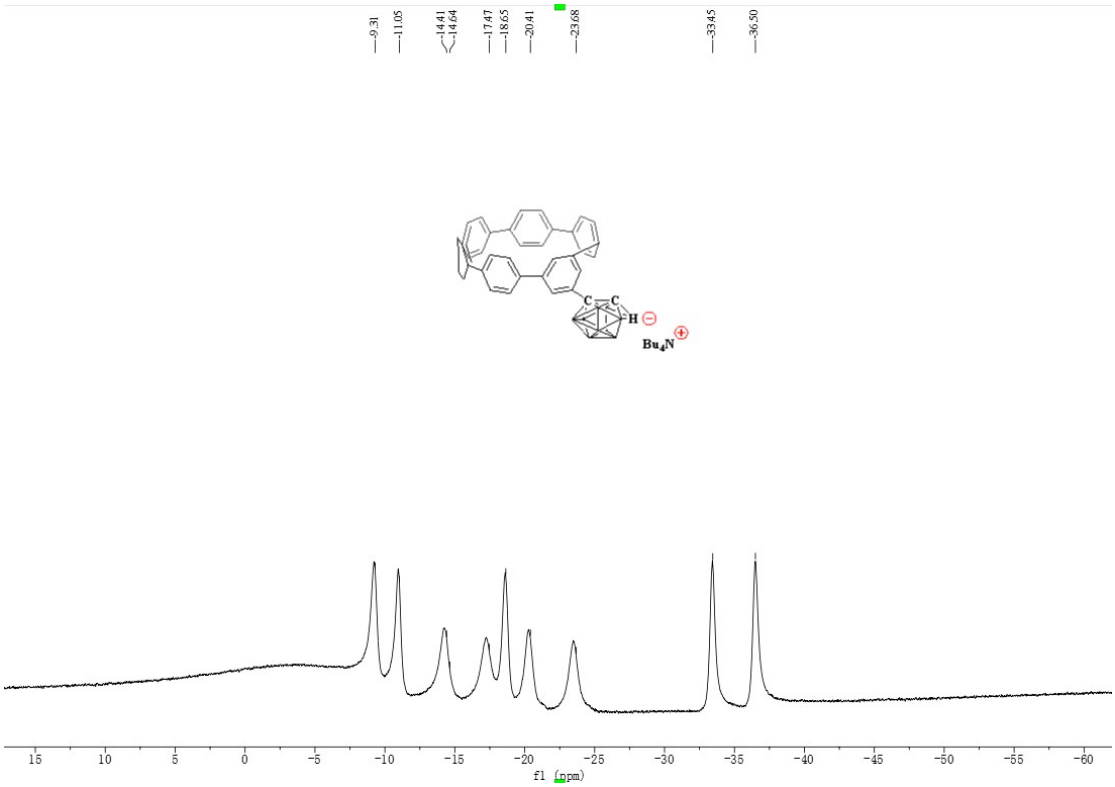


Figure S10. The ^{11}B-NMR (160 MHz, Acetone-d^6) spectrum of compound 7.

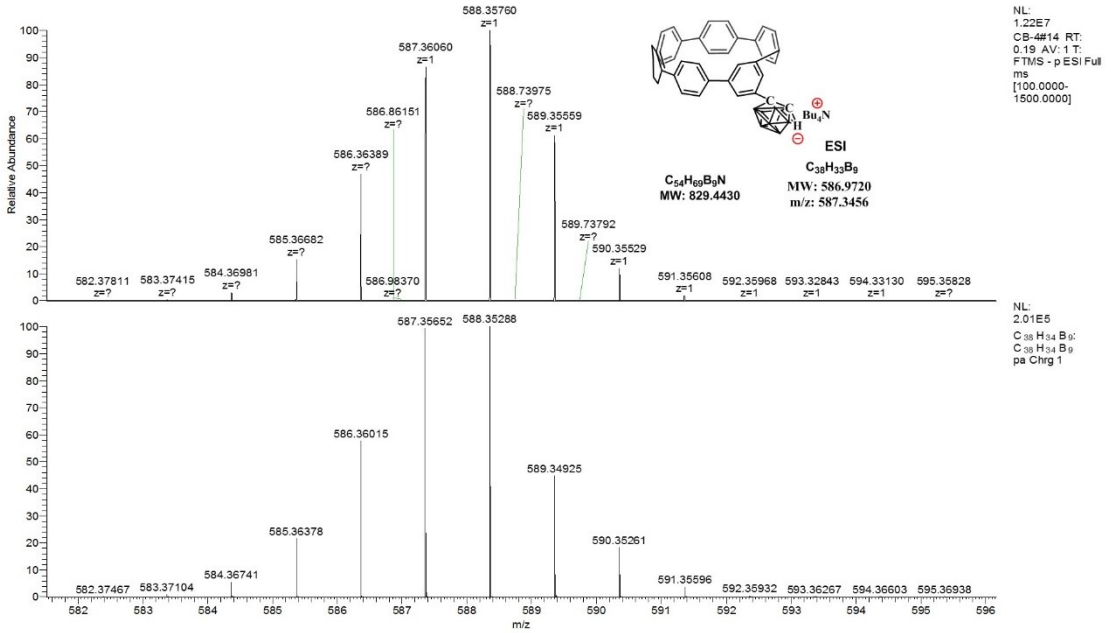


Figure.S11. The HRMS spectrum of compound 7.

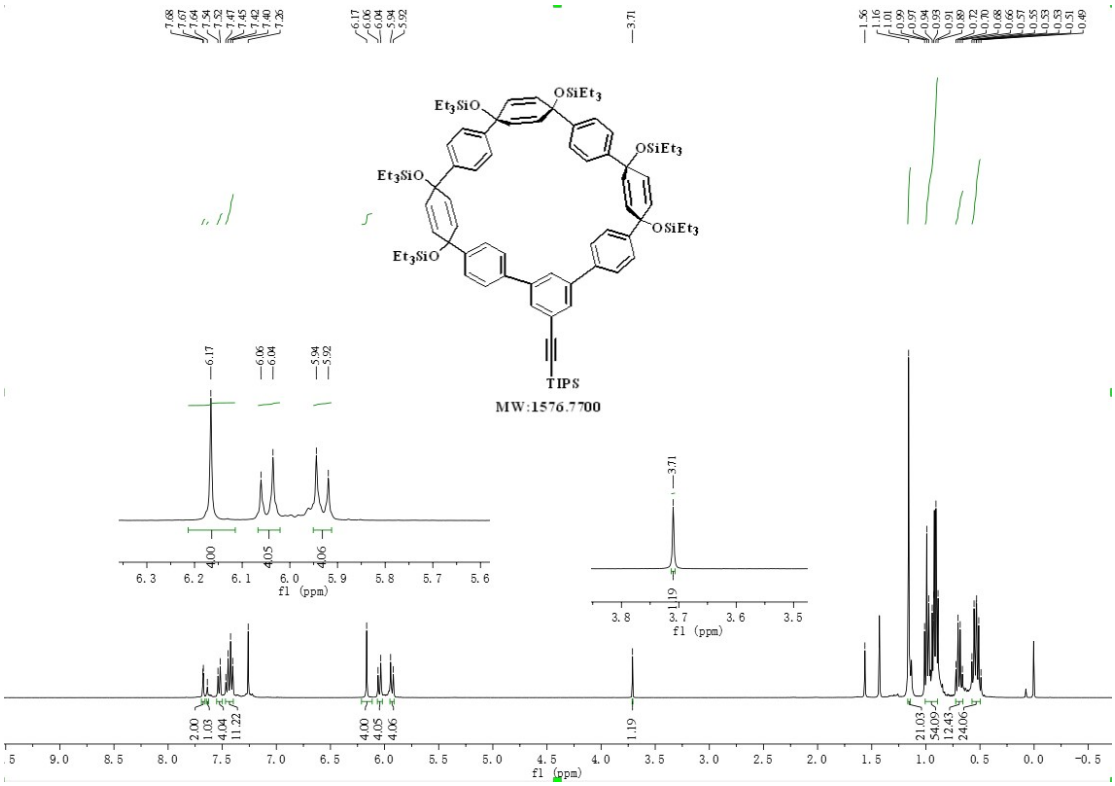


Figure S12. The ^{1}H-NMR (500 MHz, Chloroform-*d*) spectrum of compound 3a.

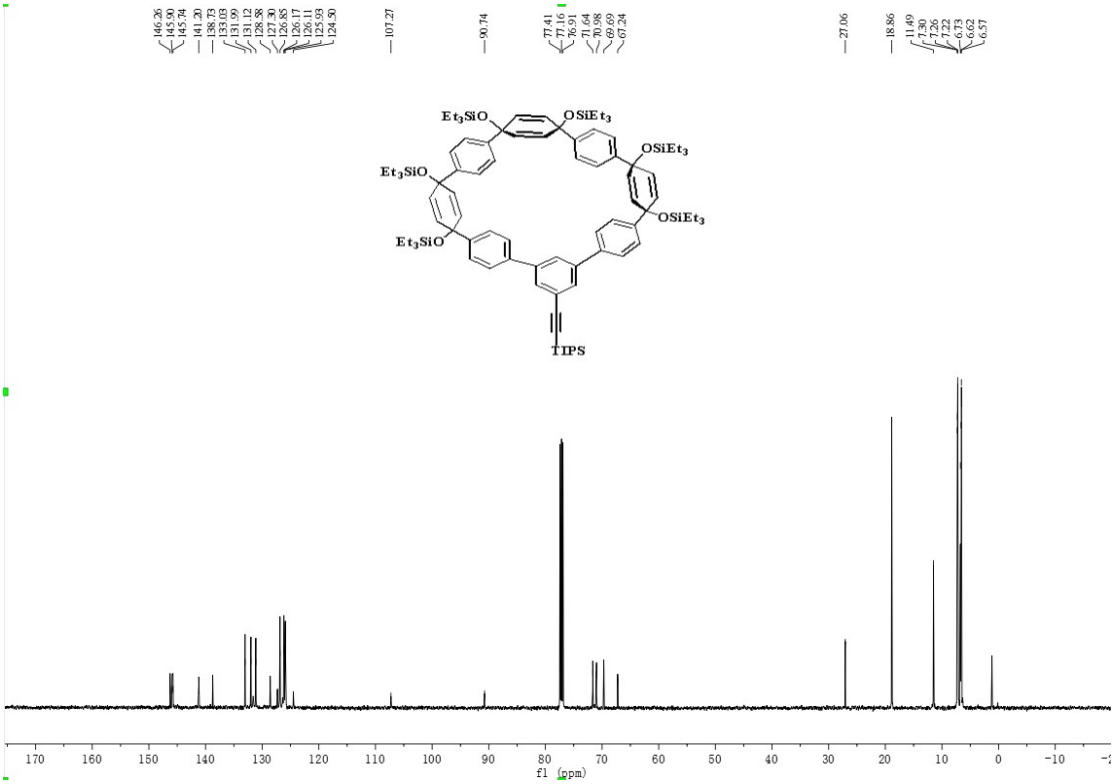


Figure S13. The ^{13}C-NMR (126 MHz, Chloroform-*d*) spectrum of compound 3a.

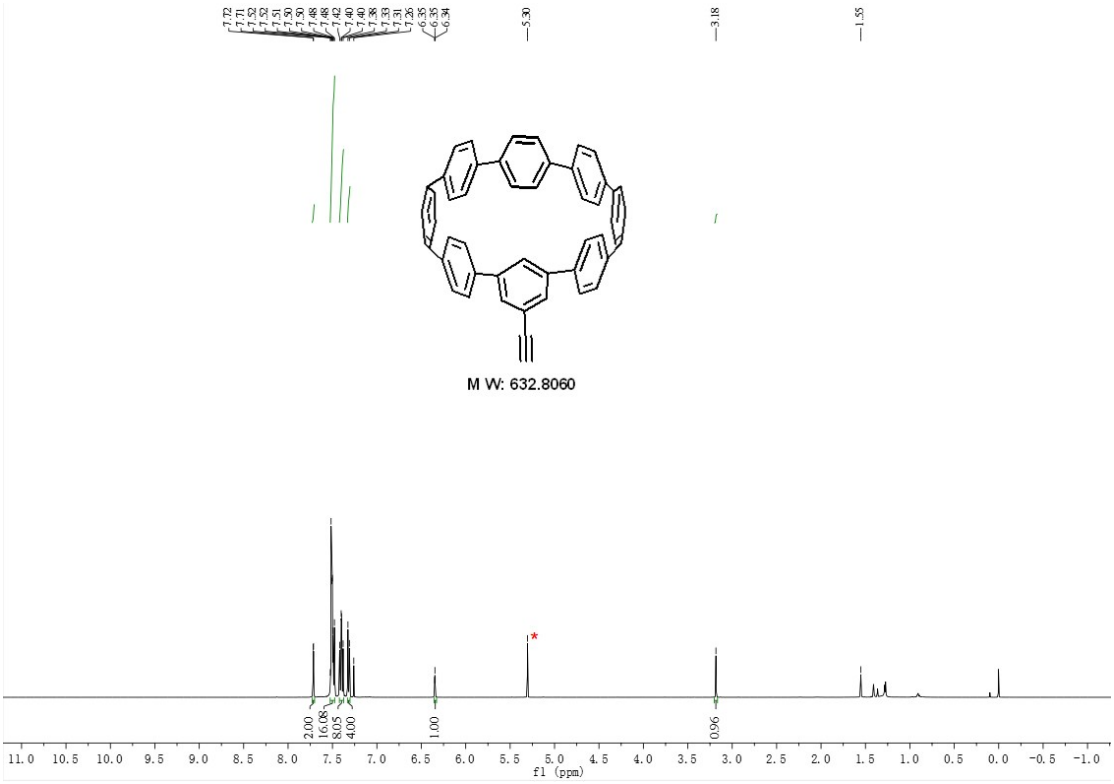


Figure S14. The ^{1}H-NMR (500 MHz, Chloroform-*d*) spectrum of compound 5a.

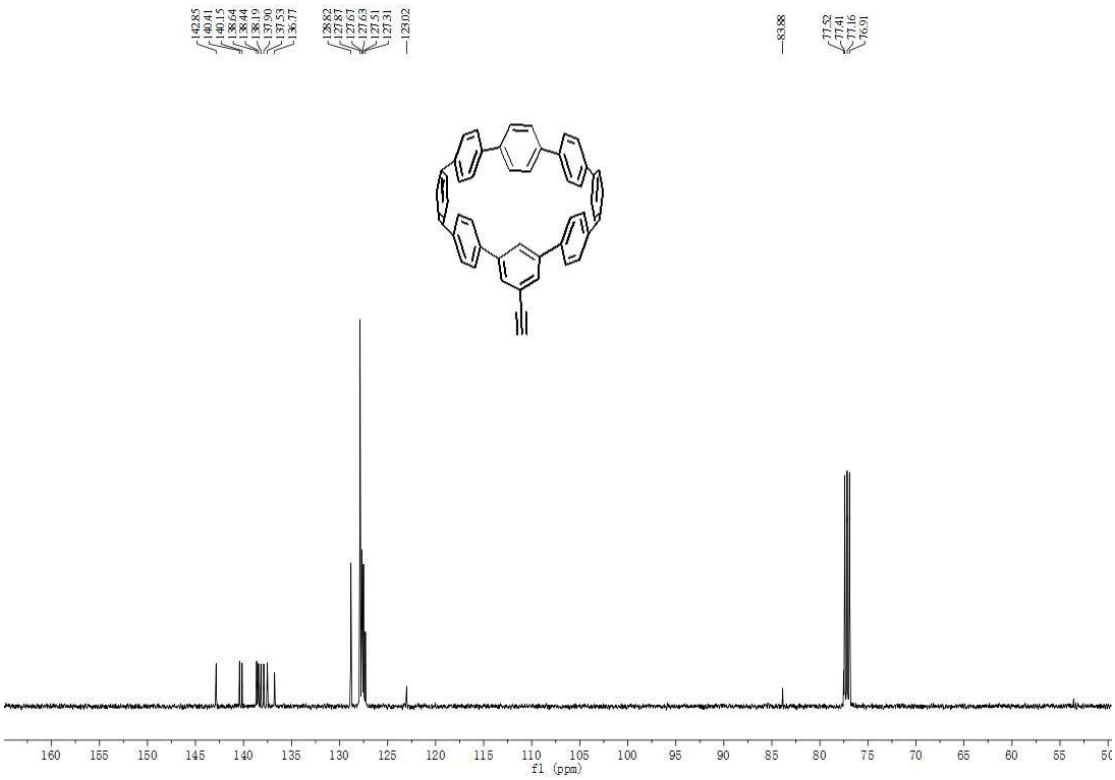


Figure S15. The ^{13}C-NMR (126 MHz, Chloroform-*d*) spectrum of compound 5a

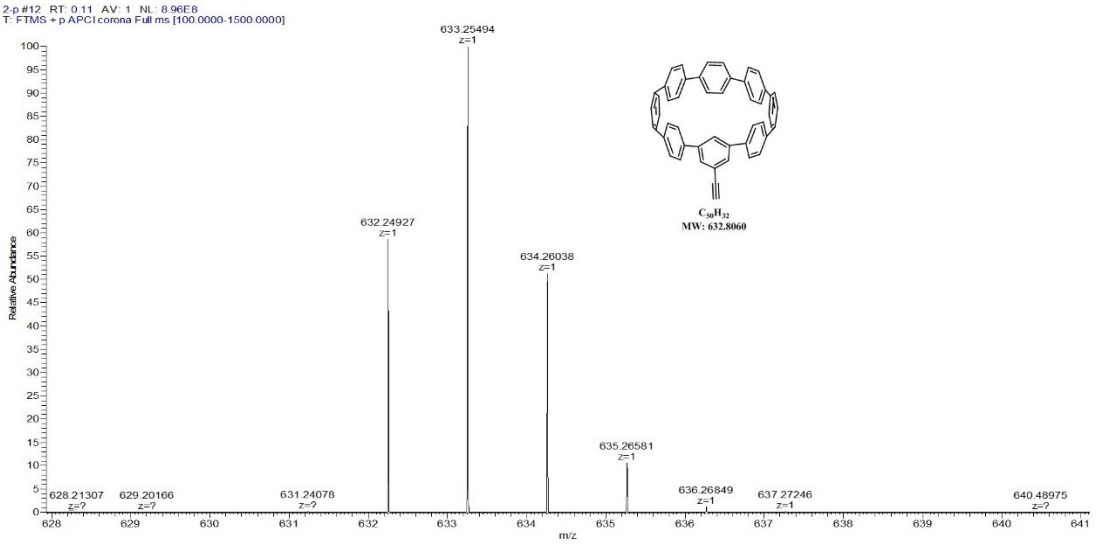


Figure S16. The HRMS spectrum of compound 5a.

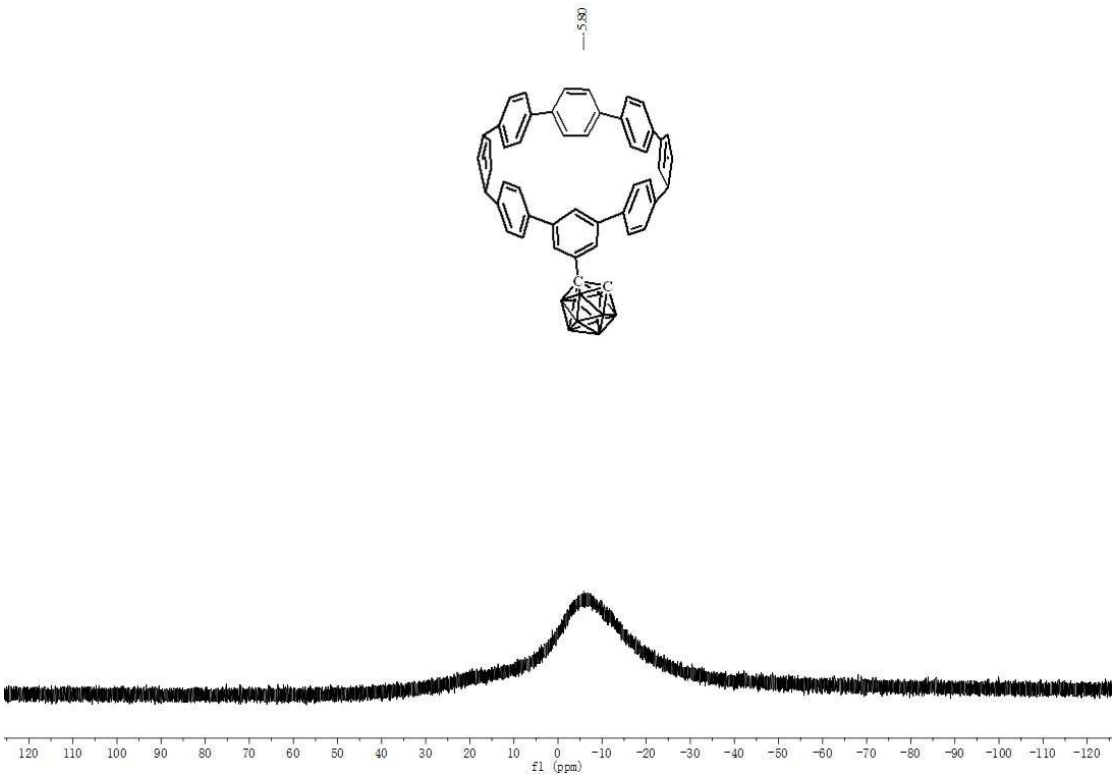


Figure S17. The ^{11}B-NMR (160 MHz, Acetone-d^6) spectrum of compound 6a.

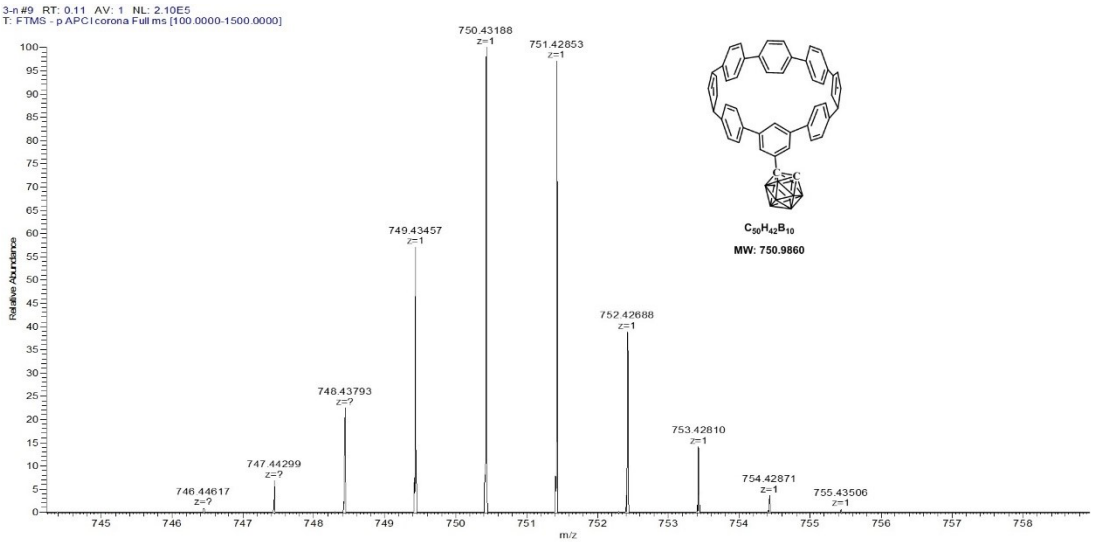


Figure S18. The HRMS spectrum of compound 6a

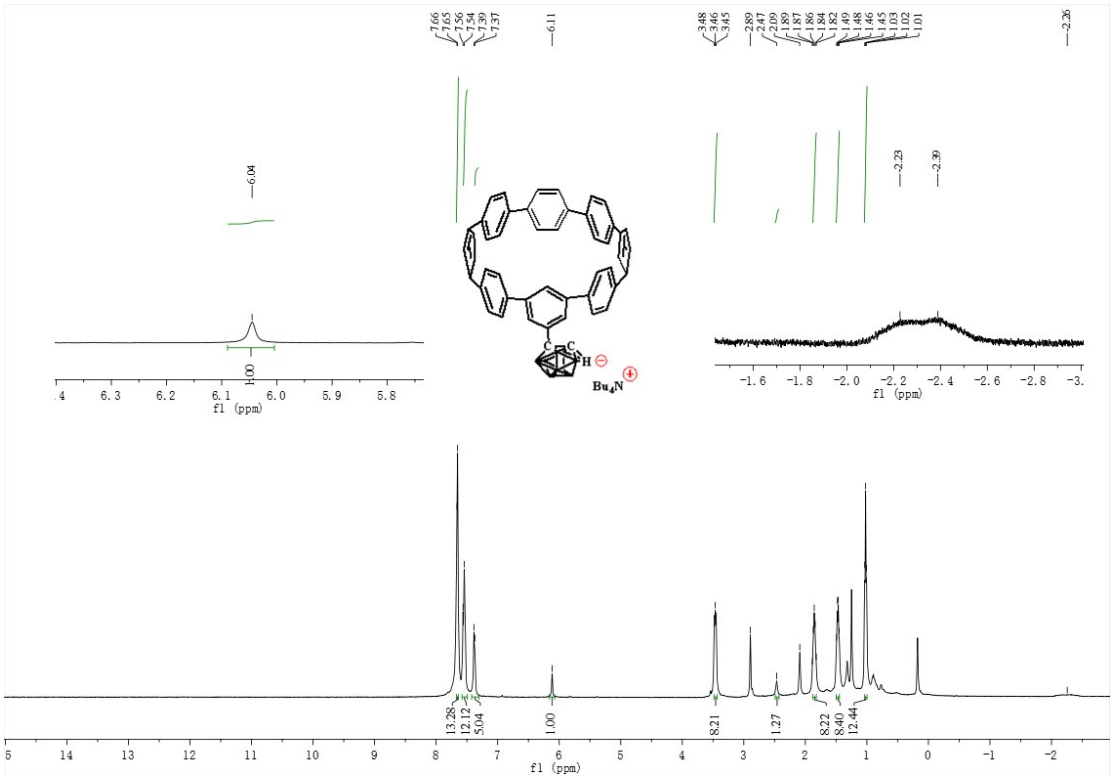


Figure S19. The ^{1}H-NMR (500 MHz, Acetone-d^{6}) spectrum of compound 7a.

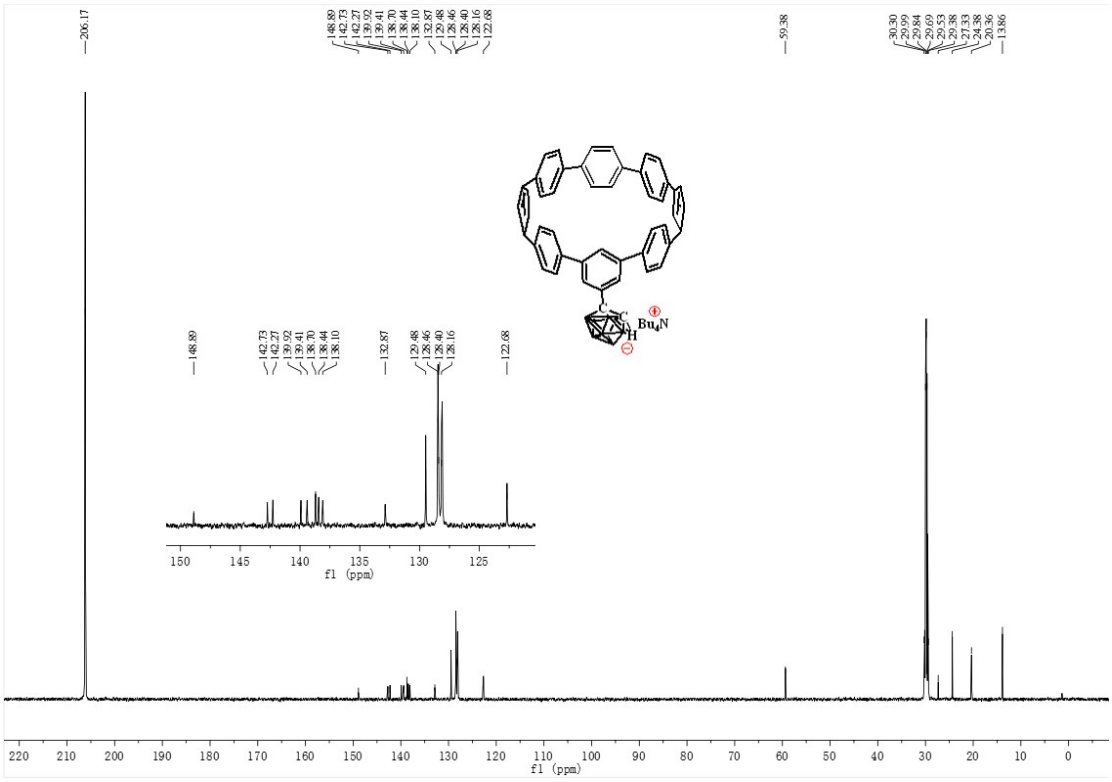


Figure S20. The ^{13}C-NMR (126 MHz, Acetone-d^{6}) spectrum of compound 7a

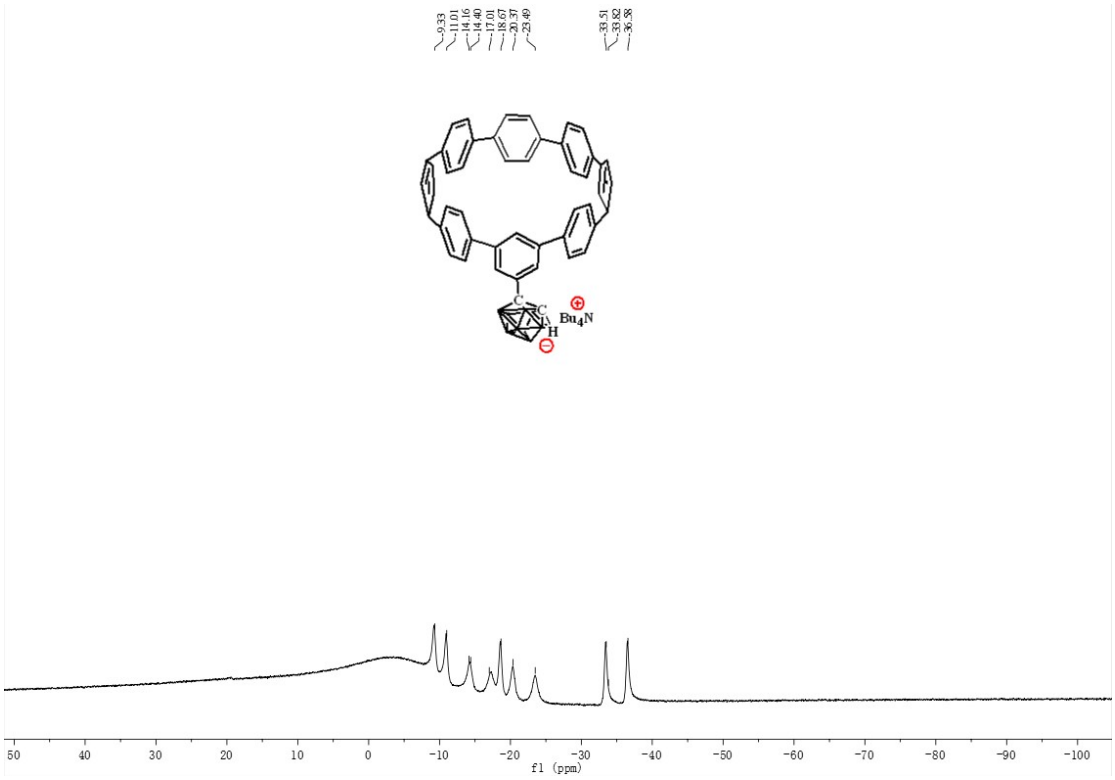


Figure S21. The ^{11}B-NMR (160 MHz, Acetone-d^6) spectrum of compound 7a.

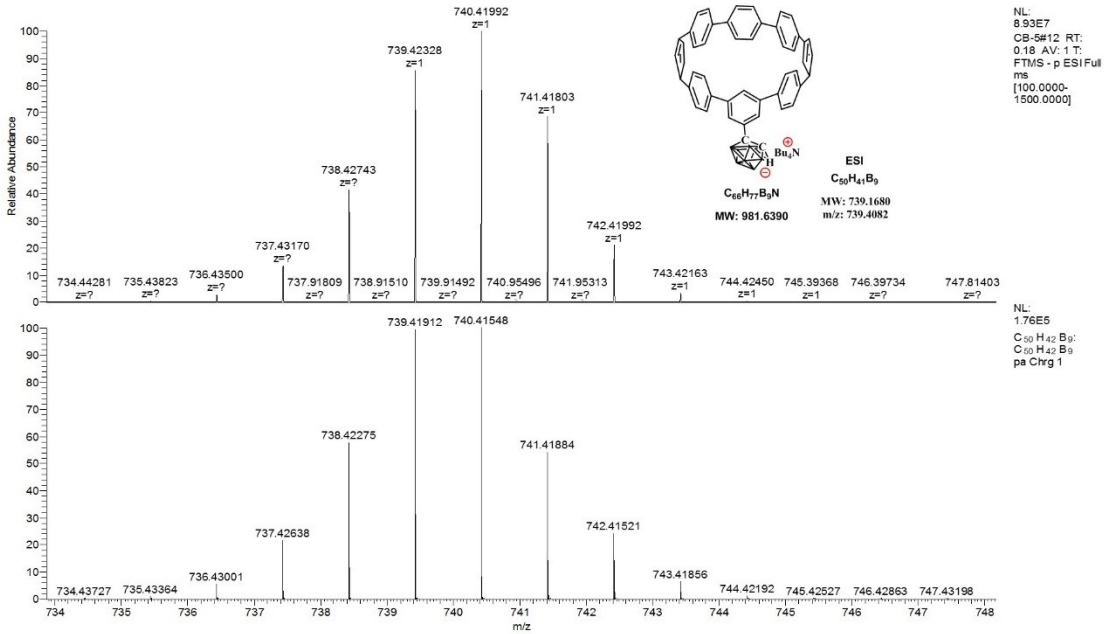


Figure S22. The HRMS spectrum of compound 7a.